GEOCHEMISTRY OF CARBONATES AND GLASS IN ALH84001.

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The stable isotope geochemistry of carbonates in SNC meteorites constrains both the characteristics of martian volatile reservoirs and the origin of secondary mineralization in these samples. We report here new ion microprobe measurements of $^{18}O/^{16}O$ in carbonates and related phases in ALH84001, supported with major-, minor-, and trace-element data on the same materials.

The background to these measurements is that carbonates in ALH84001 display a large range in oxygen isotope composition (~25‰; [1–4]), which has been ascribed either to variations in temperature [1,3,5] or Rayleigh distillation [4]. When examined in detail, variations in oxygen isotope ratio in carbonates have been shown to be correlated systematically with variations in their major element composition [1,3,4]. Although the data from several different groups are generally consistent, one difference is that ankeritic carbonates (~50% $CaCO_3$) were reported by [3] to have $\delta^{18}O_{SMOW}$ 0‰, but [4] found values of ~7‰ for carbonates in this compositional range.

We have made 82 measurements of $\delta^{18}O$ in carbonates from ALH84001, including a range of ankeritic compositions not encountered in previous studies and ~20 measurements each of all of the major populations/textural types of carbonate known in this sample. Our results confirm the overall trend of $\delta^{18}O$ with chemical composition seen in previous studies [1–4]: i.e., $\delta^{18}O$ varies by ~25‰ and tends to decrease with increasing Ca content. However, our data reveal details in the correlations between $\delta^{18}O$ and chemistry not observed in previous, smaller data sets. In particular, two distinct, offset trends occur in plots of $\delta^{18}O$ vs. major elements: (1) decreasing $\delta^{18}O$ (26→0‰) with decreasing Mg and increasing Ca and Mn in white magnesites and orange magnesio-siderites, and (2) ankerites having a large range in chemical composition ($0.45 \leq X_{Ca} \leq 0.71$) with essentially indistinguishable $\delta^{18}O$ values ($5.8 \pm 1.9‰$). There may be a subtle discontinuity in $\delta^{18}O$ and chemical composition on the first trend, between magnesites ($0.70 \leq X_{Mg} \leq 0.90$; $X_{Ca} \leq 0.05$) and magnesio-siderites ($X_{mg} < 0.70$; $0.08 \leq X_{Ca} \leq 0.44$). Our results for ankeritic carbonates are within analytical uncertainty of [4] and in disagreement with [3]. These two trends are associated with distinct carbonate textures: magnesites and magnesio-siderites are found principally in concentrically zoned "disks" [6]

and ankerites exclusively found in irregularly shaped patches.

Mn concentration is strongly correlated with Ca in ALH84001 carbonates. There are again two distinct trends, one for magnesites and magnesio-siderites and one for ankeritic carbonates, offset from each other in Ca/Mn ratio. On average, the ankerites also have higher La/Nd and Sr/Ba ratios, higher Sr and Y concentrations, and lower Ba concentrations than magnesites and magnesio-siderites. $\delta^{18}O$ is negatively correlated with La/Nd and Sr/Ba among all analyses. On average, magnesites have higher La/Y ratios and Th concentrations than other carbonate populations. All populations of carbonate have LREE-depleted rare earth patterns relative to coexisting feldspathic glass (see also [7]).

Differences in REE abundances between carbonates and feldspathic glasses are not those predicted by carbonate/silicate-melt distribution coefficients, and therefore no population of carbonate considered in this study can be consanguineous with melt from which much of the glass in ALH84001 appears to have quenched. REE and other trace element abundances vary systematically with crystallization sequence (e.g., decreasing La/Nd from ankerite→magnesio-siderite→magnesite). These variations are in the opposite direction of those predicted by fractional precipitation from a carbonic fluid based on known carbonate/fluid distribution coefficients. Given correlations between $\delta^{18}O$ and chemistry, models in which variation in $\delta^{18}O$ is due to precipitation over a range of temperatures require complex variation of fluid/carbonate distribution coefficients with temperature. Alternatively, carbonate may have precipitated from at least two chemically and isotopically distinct fluids, such that correlations among $\delta^{18}O$ and chemistry reflect different mixing proportions of end-member fluid compositions.

References: [1] Romanek et al. (1994) *Science*. [2] Valley et al. (1997) *Science*. [3] Saxton et al. (1997) *Meteoritics & Planet. Sci.* [4] Leshin et al. (1998) *GCA*; [5] Eiler et al. (1997) *Meteoritics & Planet. Sci.* [6] Mittlefehldt (1994) *Meteoritics*; [7] Wadhwa and Crozaz (1996) *LPS XXVII*.